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(54)【発明の名称】 耐炎性ポリエステル樹脂組成物

(57)【要約】

【課題】 接炎時の有毒ガスの発生や、樹脂の溶融落下による火災の拡大という問題のない樹脂製品を得ることができる、優れた耐炎性ポリエステル樹脂組成物を提供する。

【解決手段】 ポリエステル樹脂に、フェノール性水酸基を有する芳香族ジカルボン酸成分を全酸成分に対して2モル%以上共重合させ、かつ、リン化合物を、リン原子の重量としてポリエステル樹脂に対して500ppm以上含有させる。

【特許請求の範囲】

【請求項1】 ジカルボン酸成分および/またはジカルボン酸以外のエステル形成性二官能性カルボン酸成分とジオール成分とから構成されるポリエステル樹脂とリン化合物とからなる組成物であって、フェノール性水酸基を少なくとも1個以上有する芳香族ジカルボン酸成分が、全酸成分に対して2モル%以上共重合し、かつ、リン化合物が、リン原子の重量としてポリエステル樹脂に対して500ppm以上含有していることを特徴とする耐炎性ポリエステル樹脂組成物。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、接炎時に熔融落下を起こし難く、火災防止効果に優れた耐炎性ポリエステル樹脂組成物に関するものである。

【0002】

【従来の技術】 ポリエチレンテレフタレート（以下PETと略称する）に代表されるポリエステルはその優れた機械的特性及び化学的特性のため、衣料用、産業用等の繊維のほか、磁気テープ用、写真用、コンデンサー用等のフィルムあるいはボトル等の成形物用として広く用いられている。

【0003】 ところで、近年、火災防止の観点から合成繊維や各種プラスチック製品の耐炎性への要請が強まっている。従来、ポリエステルに耐炎性を付与する試みは種々なされており、ポリエステルにハロゲンを主体とする化合物とアンチモン化合物を併存させる方法（例えば、特開昭61-185559号公報等）が開示されている。しかし、このような方法は、ハロゲンを主体とする化合物を用いるため接炎時に有毒ガスを発生するという問題を有しており、ハロゲン化合物を含まないノンハロゲン化が求められている。

【0004】 ノンハロゲン化の方法としてポリエステルにリン化合物を含有させる方法（例えば、特開平2-17302号公報等）がある。この方法によってポリエステルに耐炎性を付与すると、接炎時に有毒ガスを発生しないという長所があるが、接炎時にリン化合物がポリエステルの熱分解を促進するために樹脂の熔融落下を助長してしまうという短所がある。接炎時に着火した樹脂が熔融落下すると、樹脂製品自体は消火しやすくなるが、樹脂製品の周囲、特に下部に可燃物が存在していると、落下した樹脂が着火源となって可燃物に引火し、火災が拡大してしまうことがあり、十分な火災防止効果が得られないという問題がある。

【0005】

【発明が解決しようとする課題】 本発明は、上記のような問題点を解決するものであって、接炎時の有毒ガスの発生や、樹脂の熔融落下による火災の拡大という問題のない、優れた耐炎性ポリエステル樹脂組成物を提供することを目的とするものである。

【0006】

【課題を解決するための手段】 すなわち、本発明の要旨は、次の通りである。ジカルボン酸成分および/またはジカルボン酸以外のエステル形成性二官能性カルボン酸成分とジオール成分とから構成されるポリエステル樹脂とリン化合物とからなる組成物であって、フェノール性水酸基を少なくとも1個以上有する芳香族ジカルボン酸成分が、全酸成分に対して2モル%以上共重合し、かつ、リン化合物が、リン原子の重量としてポリエステル樹脂に対して500ppm以上含有していることを特徴とする耐炎性ポリエステル樹脂組成物。

【0007】

【発明の実施の形態】 以下、本発明を詳細に説明する。本発明の組成物を構成するポリエステル樹脂には、フェノール性水酸基を少なくとも1個以上有する芳香族ジカルボン酸成分が、全酸成分の2モル%以上共重合されていることが必要である。フェノール性水酸基は、通常のカルボキシル基とはエステル結合を形成しないため、このような水酸基を有する芳香族ジカルボン酸がポリエステル中に共重合されていると、フェノール性水酸基がポリエステルの側鎖に残ったポリエステル樹脂となる。この側鎖に残ったフェノール性水酸基は、接炎時の高温下でラジカルを発生して架橋構造を作り、ポリエステル樹脂が熔融落下するのを抑制する働きがある。フェノール性水酸基を少なくとも1個以上有する芳香族ジカルボン酸成分の具体例としては、5-ヒドロキシイソフタル酸（以下HIPAと略称する）、4-ヒドロキシフタル酸（以下HPAと略称する）、2,5-ジヒドロキシ-1,4-ベンゼンジカルボン酸等が挙げられる。

【0008】 このような成分の共重合量は全酸成分に対して2モル%以上とすることが必要である。この量が2モル%未満では、接炎時の高温下においてラジカル発生による架橋構造の発達が不十分なものとなり、結果として接炎時の熔融落下を抑制する効果が不十分となる。なお、共重合量の上限については特に限定されるものではないが、共重合量が多くなるとポリエステルの熔融粘性が高くなり、熔融重合時に重合度を高めることが困難となる場合があるので、概ね20モル%以下とするのが好ましい。

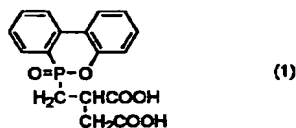
【0009】 本発明のポリエステル樹脂を構成するジカルボン酸成分、エステル形成性二官能性カルボン酸成分、およびジオール成分については、用途に応じて適宜選択すればよい。例えば、繊維やフィルム等のように高融点、高結晶性が必要とされる用途では、芳香族ジカルボン酸成分としてテレフタル酸（以下TPAと略称する）や2,6-ナフタレンジカルボン酸、脂肪族ジオール成分としてエチレングリコール（以下EGと略称する）や1,4-ブタンジオール（以下BDと略称する）を用いることができる。また、バインダー繊維や接着剤、塗料のような用途であれば、ジカルボン酸成分としてTPAとイソフタル酸

(以下IPAと略称する)、またはアジピン酸(以下ADと略称する)、セバシン酸等の脂肪族ジカルボン酸等を併用し、脂肪族ジオール成分としてEGとBD、ネオペンチルグリコール等を併用することにより、融点、結晶性等の物性を目的の範囲にコントロールしたポリエステル樹脂とすることができる。また、上記のようなジカルボン酸成分、脂肪族ジオール成分以外に、p-オキシ安息香酸のエチレンオキサイド付加体等の二官能性芳香族カルボン酸、ε-カプロラクトン(以下CLと略称する)やδ-バレロラクトン等の二官能性脂肪族カルボン酸誘導体、ビスフェノールAやビスフェノールSのエチレンオキサイド付加体等の芳香族ジオール、1,4-シクロヘキサジメタノール等の脂環族ジオールを用いることもできる。

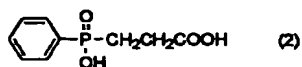
【0010】本発明の耐炎性ポリエステル樹脂組成物は、リン化合物をリン原子の重量としてポリエステル樹脂に対して500ppm以上となるように含有していることが必要である。リン化合物をポリエステル樹脂に含有させると、接炎時にリン化合物が分解し、生成するリン酸層が保護被膜となって酸素を遮断し、かつ、その脱水作用によりポリエステルの炭化を促進し、耐炎性を付与する効果がある。

【0011】本発明の樹脂組成物に含有させるリン化合物としては、有機、無機いずれのリン化合物でも適用できるが、安全性、熱的安定、ポリエステル樹脂との相溶性等の観点から、リン酸エステル誘導体、ホスホン酸誘導体、ホスフィン酸誘導体、ホスフィンオキシド誘導体等の5価の有機リン化合物が好ましい。特に、9, 10-ジヒドロ-9-オキサ-10-ホスファフェナントレン-10-オキシドのイタコン酸付加体(下記構造式(1)、以下PPIと略称する)や、(2-カルボキシエチル)フェニルホスフィン酸(下記構造式(2)、以下CPPと略称する)、または(2-カルボキシエチル)メチルホスフィン酸(下記構造式(3)、以下CMPと略称する)のように、エステル形成性官能基を2個有する有機リン化合物は、ポリエステルの重合工程において添加することにより、ポリエステル樹脂中に共重合することが可能であり、成形、紡糸等の溶融加工工程での操作性向上、製品の物性向上、耐久性の向上等の面で好ましい。

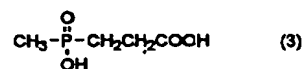
【化1】



【化2】



【化3】



【0012】このようなリン化合物の含有量は、リン原子としてポリエステル樹脂に対して500ppm以上となるようにする必要があり、好ましくは1,000ppm以上とするのがよい。リン化合物の量が500ppm未満では、ポリエステルの耐炎性能が不十分となる。添加量の上限については、特に限定されるものではないが、あまり多くすると得られるポリエステル樹脂組成物の物理的性質が損なわれたり、加工時にリン化合物がブリードアウトして操作性が低下したりすることがあるため、概ね40,000ppm以下とするのが好ましい。

【0013】本発明の耐炎性ポリエステル樹脂組成物は、例えば次のような方法により得ることができる。まず、温度230～250℃で窒素ガス制圧下、ビス-(β-ヒドロキシエチル)テレフタレートおよび/またはその低重合体(以下PETオリゴマーと略称する)の存在するエステル化反応槽に、グリコール成分/酸成分のモル比1.1～2.0のEGとTPAのスラリーを添加し、滞留時間7～8時間で、エステル化反応物を得る。このエステル化反応物を重合反応缶に移送し、HIPA等のフェノール性水酸基を有する芳香族ジカルボン酸と、前記構造式(1)～(3)に示されるようなリン化合物、および重合触媒を所定量添加して、温度230～250℃で、0.5～2時間エステル化反応を行う。その後、重合反応缶の温度を260～280℃に升温し、0.01～13.3hPaの減圧下にて、所定の極限粘度となるまで重縮合反応を行う。ポリエステル樹脂の極限粘度は、用途に応じて適宜選択すればよいが、特に製品の強度を高め、溶融成型時の加工性を良好なものとするためには0.45以上とするのが好ましい。

【0014】重縮合反応は、通常、重縮合反応触媒の存在下で行われ、従来一般に用いられているアンチモン、ゲルマニウム、スズ、チタン、コバルト等の金属の化合物が好適に用いられる。また、効果を阻害しない範囲であれば、ヒンダードフェノール系化合物のような抗酸化剤、コバルト化合物、蛍光剤、染料のような色調改良剤、顔料等の添加物を含有させてもよい。

【0015】こうして得られた耐炎性ポリエステル樹脂組成物は、通常のPETと同様に溶融成形、溶融紡糸等の加工が可能であり、耐炎性を有する成型品、繊維製品とすることができる。そして、これらの製品は接炎時に溶融落下を起こし難いため、周囲に可燃物が存在する状況下で接炎されても、溶融落下して他の可燃物に引火することがなく、優れた火災防止効果が得られる。

【0016】

【作用】本発明のポリエステル樹脂組成物が耐炎性を有し、かつ接炎時に溶融落下を起こし難く、火災防止効果に優れている理由として、本発明者は次のように考えている。本発明の樹脂組成物を構成するポリエステル樹脂

には、リン化合物を含有しているため、接炎時にリン化合物が分解し、生成するリン酸層が保護被膜となって酸素を遮断し、かつ、その脱水作用によりポリエステル樹脂の炭化を促進し、ポリエステル樹脂の燃焼を阻害する効果がある。また、本発明の耐炎性ポリエステル樹脂組成物には、フェノール性水酸基を有する芳香族ジカルボン酸が共重合されている。この分子中のフェノール性水酸基部分はポリエステル樹脂の主鎖を構成する成分の一つである通常のカルボキシル基とはエステル結合を形成しないが、分子中のジカルボン酸部分はポリエステル樹脂の主鎖を構成するもう一つの成分であるジオールと反応し、エステル結合を形成してポリエステル樹脂の分子鎖中に組み込まれる。そのため、フェノール性水酸基を側鎖に有するポリエステル樹脂となる。このフェノール性水酸基は、ポリエステル樹脂の重合時や溶融加工時程度の温度では反応しないが、接炎時の高温雰囲気下でラジカルを発生して分子間で架橋構造を作るため、リン化合物によってポリエステル樹脂の分解が促進されても、樹脂の溶融粘度が低下しにくくなり、接炎時の溶融落下を抑制することが可能となる。

【0017】

【実施例】次に、本発明を実施例により具体的に説明する。なお、例中の特性値の測定法は、次のとおりに行った。

(a) 極限粘度 ($[\eta]$)

フェノールと四塩化エタンとの等重量混合溶媒を用い、温度20℃で測定した。

(b) ポリエステルの組成

日本電子社製NMR JNM-LA4000型で測定した。

(c) リン原子の含有量

リガク社製蛍光X線スペクトロメータ 3270型にて測定した。

(d) 耐炎性

UL94規格に準じて燃焼性試験を行い、V-1以上を合格とした。

【0018】実施例1

PETオリゴマーの存在するエステル化反応缶にTPAとEGのスラリー（モル比1/1.6）を連続的に供給し、温度250℃、圧力0.1MPaGの条件で反応させ、滞留時間を8時間として、反応率95%のエステル化物を連続的に得た。次いで、エステル化物を重縮合反応缶に移送し、表1に示したモル比となるようにリン化合物としてPPI、フェノール性水酸基を有する芳香族ジカルボン酸としてHIPAを添加し、重縮合触媒として三酸化アンチモンを 2×10^{-4} モル/酸成分モル添加し、温度250℃、圧力0.1MPaGの条件で攪拌しながらエステル化反応を30分行った。次いで反応器の温度を30分で270℃に昇温し、反応器内の圧力を徐々に減じて70分後に1.2hPa以下にした。この条件下で攪拌しながら重縮合反応を2時間行い、表1に示す特性を有するポリエステル樹脂を得た。

【0019】実施例2

IPAとEGのスラリー（モル比1/3）を攪拌装置と充填塔を備えた反応缶に投入し、常圧下で攪拌しながら反応温度200℃にて、生成してくる水を反応系外に除去しつつ5時間エステル化反応を行い、反応率95%のエステル化物(A)を得た。また、PETオリゴマーの存在するエステル化反応缶にTPAとEGのスラリー（モル比1/1.6）を連続的に供給し、温度250℃、圧力0.1MPaGの条件で反応させ、滞留時間を8時間として、反応率95%のエステル化物(B)を連続的に得た。次いで、表1に示したモル比となるように、エステル化物(A)、(B)を重縮合反応缶に移送し、表1に示したモル比となるようにCPPとHIPAを添加し、重縮合触媒として三酸化アンチモンを 2×10^{-4} モル/酸成分モルを添加し、温度250℃、圧力0.1MPaGの条件で攪拌しながらエステル化反応を30分行った。次いで反応器の温度を30分で270℃に昇温し、反応器内の圧力を徐々に減じて70分後に1.2hPa以下にした。この条件下で攪拌しながら重縮合反応を3時間行い、表1に示す特性を有するポリエステル樹脂を得た。

【0020】実施例3

PETオリゴマーの存在するエステル化反応缶にTPAとEGのスラリー（モル比1/1.6）を連続的に供給し、温度250℃、圧力0.1MPaGの条件で反応させ、滞留時間を8時間として、反応率95%のエステル化物を連続的に得た。次いで、エステル化物を重縮合反応缶に移送し、表1に示したモル比となるようにCMP、5-HIPA、CL、BDを添加し、重縮合触媒として、テトラブチルチタネートを 2×10^{-4} モル/酸成分モル添加し、温度200℃、圧力0.1MPaGの条件で攪拌しながらエステル化反応を1時間行った。次いで反応器内の温度を30分で240℃に昇温し、反応器内の圧力を徐々に減じて70分後に1.2hPa以下にした。この条件下で攪拌しながら重縮合反応を3時間行い、表1に示す特性を有するポリエステル樹脂を得た。

【0021】実施例4、5、6、比較例1、2

フェノール性水酸基を有する芳香族ジカルボン酸の種類、共重合量、およびリン化合物の種類、含有量を表1に示すように種々変更した以外は、実施例1と同様に行った。なお、実施例6では、リン化合物としてトリフェニルホスフェート（以下TPPと略称する）を用い、重合時にポリエステル樹脂に対して表1記載の重量%となる量を添加して重合し、ポリエステル樹脂中に含有させた。

【0022】実施例7、比較例3、4

ポリエステル組成、フェノール性水酸基を有する芳香族ジカルボン酸の共重合、およびリン化合物の種類、含有量を表1に示すように種々変更した以外は、実施例3と同様に行った。なお、実施例7、比較例3、4では、リン化合物としてTPPを用い、重合時にポリエステル樹脂に対して表1記載の重量%となる量を添加して重合し、ポリエステル樹脂中に含有させた。実施例および比較例で得られたポリエステルの特性値を表1にまとめて示す。

ルボン酸の共重合が少ないために、接炎時の溶融落下が激しく、UL94規格に準じた燃焼性試験において綿着火を起こした。また、比較例2および4では、リン化合物の含有量が少ないために耐炎性が不十分なものであった。

【0026】

【発明の効果】本発明によれば、接炎時の有毒ガスの発生や、樹脂の溶融落下による火災の拡大という問題がなく、優れた火災防止効果を有する樹脂製品を得ることができる耐炎性ポリエステル樹脂組成物が提供される。

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(72)Inventor : TOKUTAKE MASAHIRO

(54) FLAME-RETARDANT POLYESTER RESIN COMPOSITION

(57)Abstract:

PROBLEM TO BE SOLVED: To provide an excellent flame-retardant polyester resin composition capable of obtaining a resin product free from problems of emission of a toxic gas in contacting with flame and enlarging fire due to dropping of a melt resin.

SOLUTION: This resin composition includes a polyester obtained by copolymerizing ≥ 2 mol.% based on whole acid component of an aromatic dicarboxylic acid having a phenolic hydroxyl to a polyester resin and ≥ 500 ppm of a phosphorus compound as a weight of the phosphorus atom to the polyester resin.

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[Claim(s)]

[Claim 1] the aromatic series dicarboxylic acid component which is the constituent which consists of polyester resin which consists of a dicarboxylic acid component, and/or the ester plasticity bifunctional carboxylic-acid components and diol components other than dicarboxylic acid, and phosphorus compounds, and has at least one or more phenolic hydroxyl groups -- all acid components -- receiving -- more than 2 mol % -- the flame resistance polyester resin constituent characterized by copolymerizing and phosphorus compounds containing 500 ppm or more to polyester resin as weight of the Lynn atom.

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention cannot cause melting fall easily at the time of ****, and relates to the flame resistance polyester resin constituent excellent in the fire prevention effectiveness.

[0002]

[Description of the Prior Art] The polyester represented by polyethylene terephthalate (it calls for short Following PET) is widely used as objects for moldings, such as films the object for magnetic tapes besides fiber, such as an object for garments, and industrial use, the object for photographs, for capacitors, etc., or a bottle, for the outstanding mechanical property and chemical property.

[0003] By the way, the request from a viewpoint of fire prevention to the flame resistance of a synthetic fiber or various plastics has become strong in recent years. Conventionally, various attempts which give flame resistance to polyester are made, and the methods (for example, JP,61-185559,A etc.) of making the compound which makes a halogen a subject at polyester, and an antimony compound coexist are indicated. However, in order to use for such an approach the compound which makes a halogen a subject, it has the problem of generating a toxic gas, at the time of ****, and non halogenation which does not contain a halogenated compound is called for.

[0004] There are methods (for example, JP,2-17302,A etc.) of making polyester contain phosphorus compounds as the approach of non halogenation. When flame resistance is given to polyester by this approach, there is the advantage in which a toxic gas is not generated, at the time of ****, but in order that phosphorus compounds may promote the pyrolysis of polyester at the time of ****, there is demerit in which melting fall of resin will be promoted. If the resin lit at the time of **** carries out melting fall, it will become easy to extinguish the resin product itself, but when the combustible exists in the perimeter of a resin product, especially the lower part, the resin which fell serves as an ignition source and it ignites to a combustible, and a fire

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may be expanded and there is a problem that sufficient fire prevention effectiveness is not acquired.

[0005]

[Problem(s) to be Solved by the Invention] This invention solves the above troubles and aims at offering the outstanding flame resistance polyester resin constituent without the problem of generating of the toxic gas at the time of ****, and expansion of the fire by melting fall of resin.

[0006]

[Means for Solving the Problem] That is, the summary of this invention is as follows. the aromatic series dicarboxylic acid component which is the constituent which consists of polyester resin which consists of a dicarboxylic acid component, and/or the ester plasticity bifunctional carboxylic-acid components and diol components other than dicarboxylic acid, and phosphorus compounds, and has at least one or more phenolic hydroxyl groups -- all acid components -- receiving -- more than 2 mol % -- the flame resistance polyester resin constituent characterized by copolymerizing and phosphorus compounds containing 500 ppm or more to polyester resin as weight of the Lynn atom.

[0007]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail. the aromatic series dicarboxylic acid component which has at least one or more phenolic hydroxyl groups in the polyester resin which constitutes the constituent of this invention -- more than 2 mol % of all acid components -- it is required to carry out copolymerization. A phenolic hydroxyl group will serve as polyester resin with which the phenolic hydroxyl group remained in the side chain of polyester, if copolymerization of the aromatic series dicarboxylic acid which has such a hydroxyl group is carried out to the usual carboxyl group into polyester in order not to form an ester bond. The phenolic hydroxyl group which remained in this side chain generates a radical under the elevated temperature at the time of ****, makes the structure of cross linkage, and has the work which controls that polyester resin carries out melting fall. As an example of an aromatic series dicarboxylic acid component of having at least one or more phenolic hydroxyl groups, 5-hydroxy isophthalic acid (it calls for short Following HIPA), a 4-hydroxy phthalic acid (it calls for short Following HPA), 2, 5-dihydroxy -1, 4-benzene dicarboxylic acid, etc. are mentioned.

[0008] The amount of copolymerization of such a component needs to carry out to more than 2 mol % to all acid components. Less than [2 mol %], in the bottom of the elevated temperature at the time of ****, it becomes what has inadequate development of the structure of cross linkage by radical generating, and this amount becomes inadequate [the effectiveness which controls the melting fall at the time of **** as a result]. In addition, although not limited especially about the upper limit of the amount of copolymerization, since the melt viscosity of

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polyester may become high and it may become difficult to raise polymerization degree at the time of a melting polymerization if the amount of copolymerization increases, it is desirable to consider as less than [20 mol %] in general.

[0009] What is necessary is just to choose suitably according to an application about the dicarboxylic acid component which constitutes the polyester resin of this invention, an ester plasticity bifunctional carboxylic-acid component, and a diol component. For example, for high-melting and the application for which high crystallinity is needed, ethylene glycol (it calls for short Following EG) and 1,4-butanediol (it calls for short Following BD) can be used as an aromatic series dicarboxylic acid component like fiber or a film as a terephthalic acid (it calls for short Following TPA), 2 and 6-naphthalene dicarboxylic acid, and an aliphatic series diol component. Moreover, if it is an application like binder fiber, adhesives, and a coating, it can consider as the polyester resin which controlled physical properties, such as the melting point and crystallinity, in the range of target by using together aliphatic series dicarboxylic acid, such as TPA, isophthalic acid (it calling for short Following IPA) or an adipic acid (it calling for short Following AD), and a sebacic acid, etc. as a dicarboxylic acid component, and using EG, BD, neopentyl glycol, etc. together as an aliphatic series diol component. Moreover, alicycle group diols, such as aromatic series diol [, such as bifunctional aliphatic-carboxylic-acid derivatives, such as bifunctional aromatic carboxylic acid, such as an ethyleneoxide adduct of a p-oxy-benzoic acid, epsilon-caprolactone (it calls for short Following CL), and delta-valerolactone and bisphenol A, an ethyleneoxide adduct of Bisphenol S,], 1, and 4-cyclohexane dimethanol, can also be used in addition to the above dicarboxylic acid components and an aliphatic series diol component.

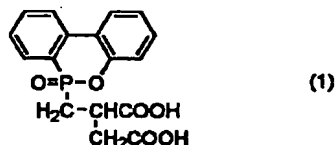
[0010] The flame resistance polyester resin constituent of this invention needs to contain phosphorus compounds so that it may be set to 500 ppm or more to polyester resin as weight of the Lynn atom. When polyester resin is made to contain phosphorus compounds, phosphorus compounds decompose at the time of ****, the phosphoric-acid layer to generate serves as a protective coating, and oxygen is intercepted, and carbonization of polyester is promoted by the dehydrating action, and there is effectiveness which gives flame resistance.

[0011] as the phosphorus compounds which the resin constituent of this invention is made to contain -- organic and inorganic -- although any phosphorus compounds are applicable, pentavalent organic phosphorous compounds, such as a phosphoric ester derivative from viewpoints, such as compatibility with safety, thermal stability, and polyester resin, a phosphonic acid derivative, a phosphinic acid derivative, and the phosphine oxide derivative, are desirable. especially -- 9 and 10-dihydro- the itaconic-acid adduct (the following structure expression (1) --) of 9-OKISA-10-phospha phenanthrene-10-oxide Following PPI -- calling for short -- phenyl (2-cull BOSHIKI ethyl) phosphinic acid (the following structure expression (2)

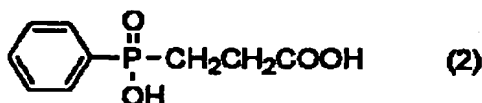
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--) It calls for short Following CPP (2-carboxy ethyl). Like methyl phosphinic acid (it calls for short the following structure expression (3) and Following CMP) By adding in the polymerization process of polyester, the organic phosphorous compound which has two ester plasticity functional groups can be copolymerized in polyester resin, and is desirable on the operation disposition in melting processing processes, such as shaping and spinning, in respect of the improvement in physical properties of a product, improvement in endurance, etc.

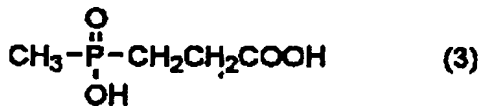
[Formula 1]



[Formula 2]



[Formula 3]



[0012] The content of such phosphorus compounds is good to make it set to 500 ppm or more to polyester resin as a Lynn atom, and to be preferably referred to as 1,000 ppm or more. The amount of phosphorus compounds becomes inadequate [the flame resistance ability of polyester] in less than 500 ppm. Although not limited especially about the upper limit of an addition, since the physical property of the polyester resin constituent obtained may be spoiled, or phosphorus compounds may carry out bleed out and operation nature may fall at the time of processing when it is made [many / not much], it is desirable to be referred to in general as 40,000 ppm or less.

[0013] The flame resistance polyester resin constituent of this invention can be obtained, for example by the following approaches. First, the slurry of EG and TPA of the mole ratios 1.1-2.0 of a glycol component / acid component is added at the temperature of 230-250 degrees C to the esterification reaction vessel in which screw-(beta-hydroxyethyl) terephthalate and/or its low-grade polymer (it is called PET oligomer for short below) exist under nitrogen gas ascendancy, and an esterification reactant is obtained in residence-time 7 - 8 hours. This

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esterification reactant is transported to a polymerization reaction can, specified quantity addition of phosphorus compounds as indicated to be aromatic series dicarboxylic acid which has phenolic hydroxyl groups, such as HIPA, to said structure-expression (1) - (3), and the polymerization catalyst is carried out, and an esterification reaction is performed at the temperature of 230-250 degrees C for 0.5 - 2 hours. Then, the temperature up of the temperature of a polymerization reaction can is carried out to 260-280 degrees C, and a polycondensation reaction is performed until it becomes predetermined limiting viscosity under reduced pressure of 0.01-13.3hPa. Although what is necessary is just to choose the limiting viscosity of polyester resin suitably according to an application, in order to raise especially the reinforcement of a product and to make good workability at the time of melting molding, carrying out to 0.45 or more is desirable.

[0014] A polycondensation reaction is usually performed under existence of a polycondensation reaction catalyst, and the compound of metals, such as antimony generally used conventionally, germanium, tin, titanium, and cobalt, is used suitably. Moreover, as long as it is the range which does not check effectiveness, additives, such as an anti-oxidant like a hindered phenol system compound, a cobalt compound, a fluorescence agent, a color tone amelioration agent like a color, and a pigment, may be made to contain. [0015] In this way, processing of melting shaping, melt spinning, etc. is possible for the obtained flame resistance polyester resin constituent like the usual PET, and it can be used as the cast and textiles which have flame resistance. And since these products cannot cause melting fall easily at the time of ****, even if they are ****(ed) under the situation that a combustible exists in a perimeter, melting fall is carried out and the fire prevention effectiveness which did not ignite to other combustibles and was excellent is acquired.

[0016]

[Function] The polyester resin constituent of this invention had flame resistance, and it was hard to cause melting fall at the time of ****, and this invention person thinks as follows as a reason excellent in the fire prevention effectiveness. Since phosphorus compounds are contained, phosphorus compounds decompose at the time of ****, the phosphoric-acid layer to generate serves as a protective coating, and oxygen is intercepted in the polyester resin which constitutes the resin constituent of this invention, and carbonization of polyester resin is promoted to it by the dehydrating action, and there is effectiveness which checks combustion of polyester resin in it. Moreover, copolymerization of the aromatic series dicarboxylic acid which has a phenolic hydroxyl group is carried out to the flame resistance polyester resin constituent of this invention. The dicarboxylic acid part in a molecule reacts with the diol which is another component from which it constitutes the principal chain of polyester resin although the usual carboxyl group which is one of the components from which the phenolic hydroxyl group part in this molecule

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constitutes the principal chain of polyester resin does not form an ester bond, forms an ester bond, and is incorporated into the chain of polyester resin. Therefore, it becomes polyester resin which has a phenolic hydroxyl group in a side chain. Although this phenolic hydroxyl group does not react at the temperature of extent at the time of the polymerization of polyester resin, and melting processing, in order to generate a radical under the elevated-temperature ambient atmosphere at the time of **** and to make the structure of cross linkage between molecules, even if disassembly of polyester resin is promoted with phosphorus compounds, it becomes possible [the melt viscosity of resin stopping being able to fall easily and controlling the melting fall at the time of ****].

[0017]

[Example] Next, an example explains this invention concretely. In addition, the measuring method of the characteristic value in an example was performed as follows.

(a) Limiting viscosity [eta]

It measured at the temperature of 20 degrees C using the same weight mixed solvent of a phenol and an ethane tetrachloride.

(b) It measured with NMR JNM[by presentation JEOL Co., Ltd.]-LA4000 mold of polyester.

(c) Fluorescence-X-rays spectrometer by content Rigaku of the Lynn atom It measured with 3270 molds.

(d) The inflammable trial was performed according to flame resistance UL94 specification, and V-1 or more was considered as success.

[0018] The esterification object of 95% of conversion was obtained continuously, having supplied continuously the slurry (mole ratios 1/1.6) of TPA and EG to the esterification reaction can with which example 1PET oligomer exists, having made it react to it on condition that the temperature of 250 degrees C, and pressure 0.1MPaG, and having used the residence time as 8 hours. Subsequently, the esterification object was transported to the polycondensation reaction can, HIPA was added as phosphorus compounds as PPI and aromatic series dicarboxylic acid which has a phenolic hydroxyl group so that it might become the mole ratio shown in Table 1, and the esterification reaction was performed for 30 minutes, having carried out 2×10^{-4} mols /, and acid component mol addition, and agitating an antimony trioxide on condition that the temperature of 250 degrees C, and pressure 0.1MPaG as a polycondensation catalyst. Subsequently, the temperature up of the temperature of a reactor was carried out to 270 degrees C in 30 minutes, and 70 minutes after reducing the pressure in a reactor gradually, it was made 1.2hPa or less. The polycondensation reaction was performed for 2 hours, agitating under these conditions, and the polyester resin which has the property shown in Table 1 was obtained.

[0019] Having supplied to the reaction can equipped with churning equipment and a packed column for the slurry (mole ratios 1/3) of EG as example 2IPA, and agitating under ordinary

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pressure, with the reaction temperature of 200 degrees C, the esterification reaction was performed for 5 hours, removing the water to generate out of the system of reaction, and the esterification object (A) of 95% of conversion was obtained. Moreover, the esterification object (B) of 95% of conversion was obtained continuously, having supplied continuously the slurry (mole ratios 1/1.6) of TPA and EG to the esterification reaction can with which PET oligomer exists, having made it react to it on condition that the temperature of 250 degrees C, and pressure 0.1MPaG, and having used the residence time as 8 hours. Subsequently, an esterification object (A) and (B) were transported to the polycondensation reaction can, CPP and HIPA were added so that it might become the mole ratio shown in Table 1, and the esterification reaction was performed for 30 minutes, having added 2×10^{-4} mols /, and acid component mol, and agitating an antimony trioxide on condition that the temperature of 250 degrees C, and pressure 0.1MPaG as a polycondensation catalyst, so that it might become the mole ratio shown in Table 1. Subsequently, the temperature up of the temperature of a reactor was carried out to 270 degrees C in 30 minutes, and 70 minutes after reducing the pressure in a reactor gradually, it was made 1.2hPa or less. The polycondensation reaction was performed for 3 hours, agitating under these conditions, and the polyester resin which has the property shown in Table 1 was obtained.

[0020] The esterification object of 95% of conversion was obtained continuously, having supplied continuously the slurry (mole ratios 1/1.6) of TPA and EG to the esterification reaction can with which example 3PET oligomer exists, having made it react to it on condition that the temperature of 250 degrees C, and pressure 0.1MPaG, and having used the residence time as 8 hours. Subsequently, the esterification object was transported to the polycondensation reaction can, CMP, 5-HIPA, and CL and BD were added so that it might become the mole ratio shown in Table 1, and the esterification reaction was performed for 1 hour, having carried out 2×10^{-4} mols /, and acid component mol addition, and agitating tetrabutyl titanate on condition that the temperature of 200 degrees C, and pressure 0.1MPaG as a polycondensation catalyst. Subsequently, the temperature up of the temperature in a reactor was carried out to 240 degrees C in 30 minutes, and 70 minutes after reducing the pressure in a reactor gradually, it was made 1.2hPa or less. The polycondensation reaction was performed for 3 hours, agitating under these conditions, and the polyester resin which has the property shown in Table 1 was obtained.

[0021] It carried out like the example 1 except having changed variously the class of aromatic series dicarboxylic acid which has examples 4, 5, and 6, the example 1 of a comparison, and 2 phenolic hydroxyl groups, the amount of copolymerization and the class of phosphorus compounds, and the content, as shown in Table 1. In addition, the polymerization of the amount which becomes weight % given in Table 1 to polyester resin at the time of a polymerization was added and carried out, using triphenyl phosphate (it calling for short Following TPP) as

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phosphorus compounds, and it was made to contain in polyester resin in the example 6.

[0022] It carried out like the example 3 except having changed variously the presentation of an example 7, the example 3 of a comparison, and 4 polyester, copolymerization of the aromatic series dicarboxylic acid which has a phenolic hydroxyl group and the class of phosphorus compounds, and the content, as shown in Table 1. In addition, the polymerization of the amount which becomes weight % given in Table 1 to polyester resin at the time of a polymerization was added and carried out, using TPP as phosphorus compounds, and it was made to contain in polyester resin in an example 7 and the examples 3 and 4 of a comparison. The characteristic value of the polyester obtained in the example and the example of a comparison is collectively shown in Table 1.

[0023]

[Table 1]

| ポリエステル樹脂の組成 | | | | | | | | | | リン化合物 | | ポリエステル特性 | | | |
|----------------------|-----|-------|-----|--------|-----|-----|-----|------------|------|-------|------------|----------|--------|--------|-------|
| ジカルボン酸または二官能性カルボン酸成分 | | | | ジオール成分 | | | | フェノール性官能成分 | | [η] | 特性値 (DL94) | | | | |
| 種類 | モル% | 重量 | モル% | 種類 | モル% | 重量 | モル% | 種類 | モル% | | | | | | |
| 1 | TPA | 80.75 | — | — | EG | 100 | — | — | HTPA | 5 | PP1 | 4.25 | 6,500 | V-1 | |
| 2 | TPA | 55.75 | TPA | 35 | EG | 100 | — | — | HTPA | 5 | CP2 | 4.25 | 6,900 | V-1 | |
| 3 | TPA | 80.75 | CL | 10 | EG | 45 | BD | 55 | HTPA | 5 | CP2 | 4.25 | 6,900 | V-1 | |
| 4 | TPA | 83 | — | — | EG | 100 | — | — | HTPA | 10 | PP1 | 7.0 | 10,100 | V-0 | |
| 5 | TPA | 84 | — | — | EG | 100 | — | — | HTPA | 15 | PP1 | 1.0 | 0.49 | 1,500 | V-1 |
| 6 | TPA | 95 | — | — | EG | 100 | — | — | HPA | 5 | TP2 | 15.0 | 0.52 | 14,300 | V-0 |
| 7 | TPA | 85 | AD | 10 | EG | 45 | BD | 55 | HTPA | 5 | TP2 | 10.0 | 0.55 | 9,900 | V-1 |
| 1 | TPA | 94.75 | — | — | EG | 100 | — | — | HTPA | 1 | PP1 | 4.25 | 6,500 | V-2 | |
| 2 | TPA | 94.75 | — | — | EG | 100 | — | — | HTPA | 5 | PP1 | 0.25 | 0.61 | 400 | V-2未測 |
| 3 | TPA | 85 | CL | 14 | EG | 45 | BD | 55 | HTPA | 1 | TP2 | 15.0 | 0.56 | 14,400 | V-2 |
| 4 | TPA | 85 | CL | 10 | EG | 45 | BD | 55 | HTPA | 5 | TP2 | 0.4 | 0.61 | 400 | V-2未測 |

表 4-10

比較例

TPA: テフタル酸, IPA: イソフタル酸, CL: 1-カルボラトール, AD: アジピン酸, EG: エチレングリコール, BD: 1,4-ブチンジオール, HTPA: 5-ヒドロキシTPA, HP: 4-ヒドロキシTPA, PP1: 9,10-ジヒドロ-9,10-メチル-9H-フラベンチン-10-オキシドのイタコン酸付加体, CP2: (2-カルボキシエチル)アミン酸, DBP: (2-カルボキシエチル)メチルホスフィン酸, TP2: トリフエノスフェート

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was obtained. When the tension test was performed for the 50cm sample the rate for 50cm/and it asked for reinforcement and ductility from the stress-strain curve about the obtained fiber using tensilon RTC[by the cage en tech company]-1210 mold, it had on-the-strength =3.15 cN/dtex, ductility =30.5%, and a good strong ductility property. Next, the obtained fiber is made into cylinder knitting fabric, and the 1g is rounded off in die length of 10.0cm, and it inserts into the wire coil of the diameter of 10.0mm, and holds at the include angle of 45 degrees, It lights by the microburner with an aperture of 0.64mm from a lower limit, when a fire source is kept away, the fire is extinguished and it asks for the count of ignition taken to repeat ignition again and for all samples to all burn, the average of the count of ignition about five samples has 4.5 times and the outstanding flame resistance, and ignition by the melting fall to the absorbent cotton put on the lower part at the time of **** was not seen.

[0025] The polyester resin constituent of examples 1-7 could not cause the melting fall at the time of **** easily, and had V-1 or more outstanding flame resistance in the inflammable trial according to UL94 specification so that clearly from Table 1. Moreover, as shown in the example of reference, the stringiness of a resin constituent was good and it was possible to have obtained fiber with the outstanding flame resistance. On the other hand, in the examples 1 and 3 of a comparison, since there was little copolymerization of the aromatic series dicarboxylic acid which has a phenolic hydroxyl group, the melting fall at the time of **** was intense, and caused cotton ignition in the inflammable trial according to UL94 specification. Moreover, since there were few contents of phosphorus compounds, the flame resistance of the examples 2 and 4 of a comparison was insufficient.

[0026]

[Effect of the Invention] According to this invention, the flame resistance polyester resin constituent which can obtain the resin product which there is no problem of generating of the toxic gas at the time of **** and expansion of the fire by melting fall of resin, and has the outstanding fire prevention effectiveness is offered.

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